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# Magnetoelastic hybrid excitations in CeAuAl<sub>3</sub>

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Nearly a century of research has established the Born–Oppenheimer approximation as a cornerstone of condensed-matter systems, stating that the motion of the atomic nuclei and electrons may be treated separately. Interactions beyond the Born–Oppenheimer approximation are at the heart of magneto-elastic functionalities and instabilities. We report comprehensive neutron spectroscopy and ab initio phonon calculations of the coupling between phonons, CEF-split localized 4f electron states, and conduction electrons in the paramagnetic regime of CeAuAl<sub>3</sub>, an archetypal Kondo lattice compound. We identify two distinct magneto-elastic hybrid excitations that form even though all coupling constants are small. First, we find a CEF–phonon bound state reminiscent of the vibronic bound state (VBS) observed in other materials. However, in contrast to an abundance of optical phonons, so far believed to be essential for a VBS, the VBS in CeAuAl<sub>3</sub> arises from a comparatively low density of states of acoustic phonons. Second, we find a pronounced anticrossing of the CEF excitations with acoustic phonons at zero magnetic field not observed before. Remarkably, both magneto-elastic excitations are well developed despite considerable damping of the CEFs that arises dominantly by the conduction electrons. Taking together the weak coupling with the simultaneous existence of a distinct VBS and anticrossing in the same material in the presence of damping suggests strongly that similarly well-developed magneto-elastic hybrid excitations must be abundant in a wide range of materials. In turn, our study of the excitation spectra of CeAuAl<sub>3</sub> identifies a tractable point of reference in the search for magneto-elastic functionalities and instabilities.

magneto-elastic coupling | f-electron materials | neutron spectroscopy | Kondo lattice materials | crystal electric field

The interactions between elementary excitations such as phonons, plasmons, magnons, or particle–hole pairs drive emergent functionalities and electronic instabilities such as multiferroic behavior (1), anomalous thermoelectric properties (2), polar order (3), or superconductivity (4). However, the interplay of the underlying energy scales, namely phonons, crystal electric field (CEF) excitations, particle–hole pairs, spin–orbit coupling, and magnetic interactions, typically tends to be of a similar strength characteristic to that of a veritable chicken-and-egg type of problem. In turn, a key question concerns the possible existence of coupling phenomena in systems featuring weak interactions in the absence of electronic instabilities, such as magnetic or multipolar order, as well as structural instabilities. In this limit the electronic degrees of freedom reduce to the CEFs as well as the conduction electrons (for the case of metals), and the Born–Oppenheimer approximation (5) may be readily expected to be valid.

Whereas the conventional properties of the CEF excitations in such a pristine environment are well documented, longstanding questions concern the formation of additional excitations beyond the single-ion level, as well as finite lifetimes and anomalous temperature dependences. Two primary mechanisms have been considered. First, phonons may create CEF transitions between

neighboring ions (6), representing an important example of so-called magneto-elastic (ME) coupling in the absence of magnetic order (7–10). Second, in metallic systems a coupling exists with particle–hole excitations (11). While various facets of the CEFs have been studied extensively, experimental information on the coupling strengths as well as the full range of properties of the CEFs is remarkably limited due to a lack of high-resolution single-crystal data (12–17).

Paramagnetic rare-earth intermetallics with weak ME coupling are particularly suited to resolve these questions, as both spin and orbital angular contributions generate the ME coupling, and the well-defined multiplet structure of the f shells makes the ME coupling tractable (18). For instance, formation of a vibronic bound state (VBS) between phonons and CEF excitations has been reported in CeAl<sub>2</sub> (19–22). Similar VBSs have also been proposed to exist in PrNi<sub>2</sub> (23), Ce<sub>3</sub>Pt<sub>23</sub>Si<sub>11</sub> (24), CePd<sub>2</sub>Al<sub>2</sub> (13, 25), and CeCuAl<sub>3</sub> (14) as well as rare-earth doped cuprates (26) and geometrically frustrated oxides (8, 15, 27). However, as the phonon density of states must be large, it is generally believed that the VBS may be formed only with weakly dispersive optical phonons. This raises the question of the origin of unexplained excitations at momentum transfers away from the  $\Gamma$  point (28), the nature of inconsistencies of presently known VBSs with light scattering (29, 30), and whether ME-hybrid modes may be

## Significance

A cornerstone of condensed-matter physics is the Born–Oppenheimer approximation, which assumes that the motion of the atomic nuclei and electrons in solids may be treated separately. We report the observation of two distinct magneto-elastic hybrid excitations of the phonons and crystal electric fields (CEF) in the paramagnetic state of the Kondo lattice compound CeAuAl<sub>3</sub>: (i) a vibronic bound state and (ii) a pronounced anticrossing. The formation of both excitations due to acoustic phonons in the presence of small coupling constants, as well as considerable damping of the CEF excitations by the conduction electrons, suggests that similar hybrid excitations must generically exist in a wide range of materials. This identifies CeAuAl<sub>3</sub> as a showcase for the development of a predictive understanding of magneto-elastic instabilities.

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The authors declare no conflict of interest.

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generic in paramagnets and driven by the full spectrum of optical and acoustic phonons (18).

On a related note, formation of an anticrossing, also referred to as level repulsion, representing a different ME-hybrid mode has been suggested at the intersection of acoustic phonons and CEF excitations in Pr and PrAl<sub>2</sub> under an applied magnetic field and the magnetically ordered state of TmVO<sub>4</sub>, where they are mediated by dipolar interactions (31–36). In comparison, a generic anticrossing in zero magnetic field between phonons and CEFs that is mediated by quadrupolar interactions in a paramagnetic state has been predicted only theoretically. Putative evidence for the latter may have been observed in the insulators PrAlO<sub>3</sub> (37) and TbVO<sub>4</sub> (38); in the rare-earth (RE) compound PrNi<sub>5</sub> the evidence is indirect (39, 40).

The formation of well-defined ME-hybrid modes is constrained by the lifetime and temperature dependence of CEF excitations, which deviates in many materials from the expected thermal population of single-ion states (41–46). In a seminal theoretical study Becker, Fulde, and Keller (BFK) (11) successfully attributed the anomalous temperature dependences of the CEF occupation to the interaction with particle–hole pairs in metallic systems. Interestingly, these interactions may mediate supercon-

ductive pairing as proposed in UPd<sub>2</sub>Al<sub>3</sub> (44, 45, 47, 48) and PrOs<sub>4</sub>Sb<sub>12</sub> (49).

In this paper we report a comprehensive single-crystal inelastic neutron scattering study of the low-lying excitations and ab initio phonon calculations in the paramagnetic state of CeAuAl<sub>3</sub> (Fig. 1A), a member of the CeTAl<sub>3</sub> series (T = Ce, Au, Pd, Pt) and thus the wider family of BaAl<sub>4</sub>-type materials (52). Early measurements of the bulk and transport properties of polycrystalline samples established CeAuAl<sub>3</sub> as a Kondo lattice compound stabilizing incommensurate antiferromagnetic order below  $T_N = 1.32$  K (50, 54). The enhancement of the linear temperature dependence of the specific heat and quadratic temperature dependence of the resistivity ( $\gamma = 227$  mJ·mol<sup>−1</sup>·K<sup>−2</sup> and  $A = 5$  μΩcm·K<sup>−2</sup>, respectively) are characteristic of a heavy Fermi liquid state. The CEF lifts the degeneracy of the Ce<sup>3+</sup>  $J = 5/2$  manifold directly as seen in the magnetic susceptibility and specific heat. However, the first and second doublets at  $T_I = 57$  K and  $T_{II} = 265$  K are split from the ground state such that they have no bearing on the bulk properties and the enhancement of the Fermi liquid ground state. An unusual feature is a reduced anisotropic thermal conductivity attributed to ME phonon scattering of the Ce ions (55).

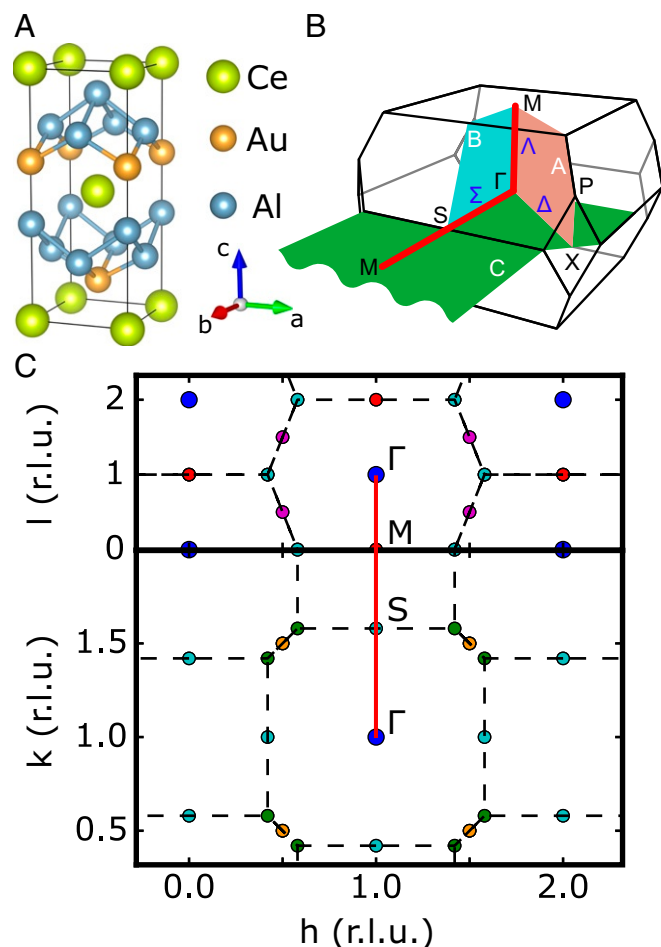
The observation of a VBS in CePd<sub>2</sub>Al<sub>2</sub> (13), a related tetragonal compound, appears to be intimately related to a structural phase transition and suggests a strong interplay of the CEF excitations and phonons in this class of systems. Indeed, time-of-flight (TOF) neutron spectroscopy revealed also a VBS in polycrystalline CeCuAl<sub>3</sub> (14) confirmed recently in single-crystal spectroscopy (56) and in slightly off-stoichiometric samples (57). Here, too, electronic excitations are assumed to hybridize with optical phonons, which results in four doublets:  $|\Gamma_6, 0\rangle$ ,  $|\Gamma_6, 1\rangle$ , and  $|\Gamma_7^{1,2}, 0\rangle$ . This suggests that the symmetry of the lattice fluctuations imparts a different character on the VBS in tetragonal compared with cubic systems. However, systematic time-of-flight neutron spectroscopy in polycrystalline CeRhGe<sub>3</sub> (58) and CeAuAl<sub>3</sub> (54) failed to detect a VBS. Moreover, the search for ME phonon softening by inelastic X-ray scattering in CeCuAl<sub>3</sub> and CeAuAl<sub>3</sub> has been inconclusive (59).

## Results

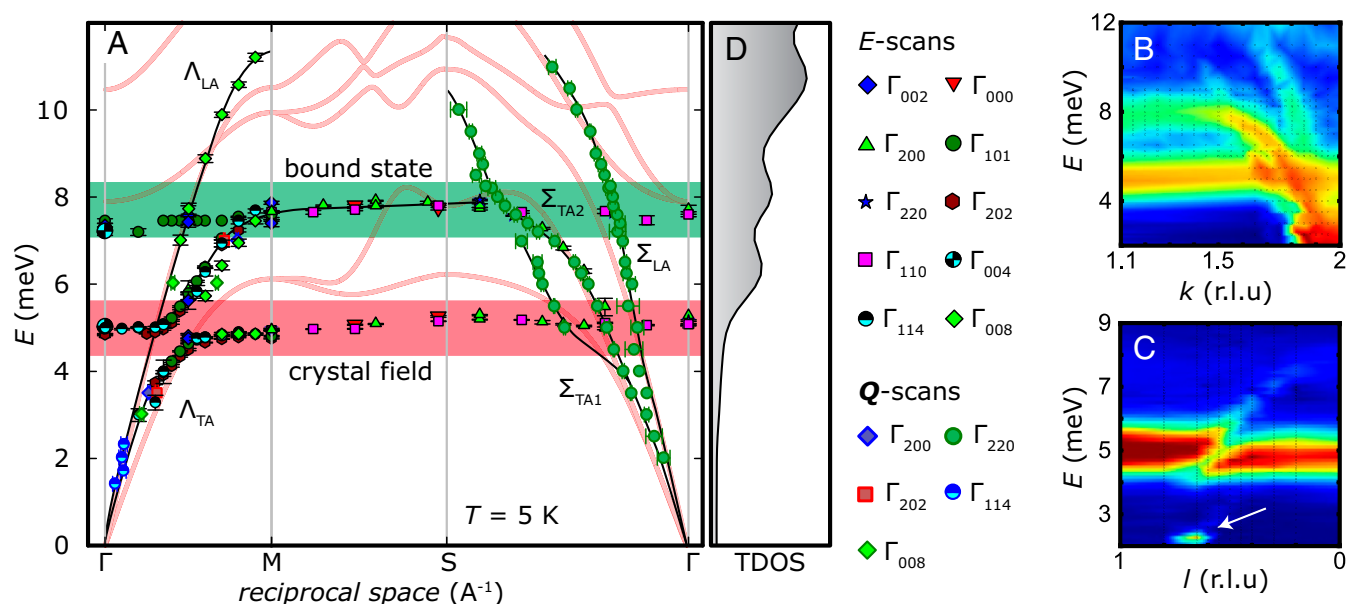
Shown in Fig. 1B is the first Brillouin zone (BZ) of the body-centered tetragonal unit cell of CeAuAl<sub>3</sub>. The relevant  $(h, k, 0)$  and  $(h, 0, l)$  planes in reciprocal space are indicated by a red line in Fig. 1B and C. Starting at the  $\Gamma$  point, this trajectory proceeded along the  $c$  axis toward the zone boundary at the  $M$  point, followed by the line connecting the  $M$  and the  $S$  points in the  $ab$  plane, before returning to the  $\Gamma$  point. Since these directions of momentum transfer do not coincide with the main crystallographic orientations of the primitive unit cell, neutrons couple to all polarizations of the phonon modes. This proves to be helpful in the interpretation of our data presented below.

An overview of the excitation spectra of CeAuAl<sub>3</sub> as a function of reduced scattering wave vector  $\mathbf{q}$  is presented in Fig. 2A. All data were recorded at a temperature of 5 K or higher, in the paramagnetic state well above  $T_N$ . For any reduced scattering vector  $q$ , the spectra feature two flat excitations, marked by red and green shading. The flat excitations are crossed by strongly dispersive phonon modes branching out of the  $\Gamma$  points. The interplay of the acoustic phonons with the flat excitations features the two main experimental findings of our study, notably (i) formation of a VBS as marked by green shading and (ii) well-resolved anticrossing of acoustic phonons with the crystal field along the  $\Gamma$  to  $M$  direction shown in Fig. 2C. Both excitations are rather distinct despite considerable broadening of the crystal-field levels with increasing temperature as shown in Fig. 3 and discussed below.

The crystal-field excitation at  $E_{CF} = 4.9$  meV (Fig. 2A, red shading) may be attributed to the transition from the  $|\Gamma_6\rangle$  ground



**Fig. 1.** Depiction of key characteristics of CeAuAl<sub>3</sub> in real and reciprocal space. (A) Crystallographic unit cell of CeAuAl<sub>3</sub>. The tetragonal BaNiSn<sub>3</sub> structure (space group  $I4mm$ , no. 107) lacks inversion symmetry (50–52). (B) Brillouin zone of a body-centered tetragonal lattice (where  $c > a$ ). High-symmetry positions are marked according to the Bilbao notation (53), where points, lines, and planes are denoted by black, blue, and white letters, respectively. (C)  $(h, k, 0)$  and  $(h, 0, l)$  planes in reciprocal space. Locations at which data were recorded are marked by a red line.



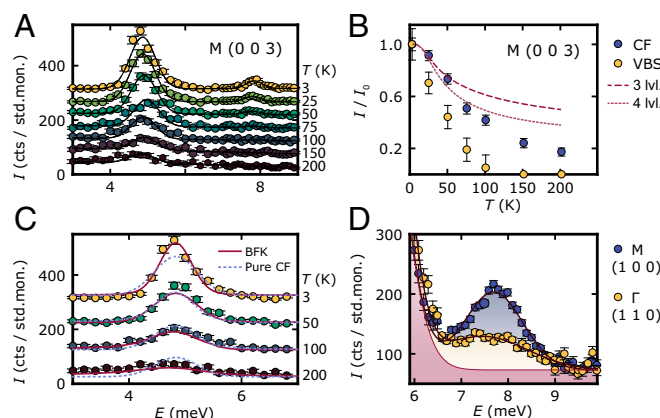
**Fig. 2.** Key characteristics of the neutron-scattering excitation spectra of single-crystal  $\text{CeAuAl}_3$  observed in reciprocal space along  $\Gamma$  to  $M$  to  $S$  to  $\Gamma$  at  $T = 5$  K. (A) Energy vs. reciprocal space map of  $\text{CeAuAl}_3$ . Data points represent the peak positions of Gaussian fits (energy scans are denoted by a black border; momentum scans are denoted by a colored border). Blue, red, and green shading denotes the Brillouin zone in which data were recorded (see Fig. 4). The plots display the location of maxima only, but not the strength of the intensities. Red lines in background represent the results of ab initio phonon calculations, where the  $f$  electrons were treated as valence electrons (60). (B) Intensity map inferred from excitation spectra recorded between  $M$  and  $\Gamma$  along  $(2, k, 0)$ . Above the crystal field excitations around 5 meV a magneto-elastic hybrid excitation emerges around 8 meV. (C) Intensity map inferred from excitation spectra recorded between  $\Gamma$  and  $M$  along  $(1, 0, l)$ . A clear anticrossing is observed. The feature marked by a white arrow represents spurious Bragg scattering. (D) Calculated phonon density of states (compare red lines in A). Maxima are observed at 6 meV, 8 meV, and 11 meV, consistent with the bound state at  $E_{VBS} = 7.9$  meV. The black line and color shading serve to guide the eye.

state to the first excited doublet  $|\Gamma_7^1\rangle$  (compare Fig. 2B). The energy of this transition is in excellent agreement with previous time-of-flight neutron spectroscopy and bulk data in a polycrystalline sample, which, however, did not allow a search for a momentum dependence (50, 54). The weak nondispersive excitation at  $E_{VBS} = 7.9$  meV (Fig. 2A, green shading) is an unexpected characteristic. It was not observed in previous time-of-flight neutron spectroscopy studies (54), probably due to the loss in spectral weight in the polycrystalline average.

The strongly dispersive excitations at the  $\Gamma$  points may be clearly attributed to acoustic phonons as they emanate from nuclear Bragg peaks. Taking into account the tetragonal crystal symmetry, a longitudinal and a transverse acoustic branch are observed along the  $\Gamma$  to  $M$  direction, labeled as  $\Lambda_{LA}$  and  $\Lambda_{TA}$ , respectively. As illustrated in Fig. 2C, these phonons display compelling evidence of an anticrossing with the crystal-field excitation at  $E_{CF}$  in the three independent Brillouin zones studied, namely (101), (202), and (114) (SI Appendix). In contrast, for the  $\Gamma$  to  $S$  direction (labeled  $\Sigma$ ) the two nondegenerate transverse acoustic phonons and a longitudinal acoustic phonon, denoted  $\Sigma_{TA1}$ ,  $\Sigma_{TA2}$ , and  $\Sigma_{LA}$ , respectively, cross the nondispersive excitations at  $E_{CF}$  and  $E_{VBS}$  without apparent interaction (Fig. 2B). We could not identify any evidence for phonons in the vicinity of the zone boundary between the  $M$  and  $S$  points, either because the intensity was too low or because they coincided with the VBS. The intensity marked by the white arrow in Fig. 2C is a so-called Currat-Axe spurion, which is a well-known artifact in triple-axis spectroscopy.

The momentum dependence of the intensity of the dispersionless excitations at  $E_{CF}$  and  $E_{VBS}$  follows from the form factor of the  $\text{Ce}^{3+}$  ion (SI Appendix, Fig. S6). This provides strong evidence that these excitations are essentially magnetic. By contrast, the strongly dispersive excitations at the  $\Gamma$  points are essentially due to nuclear scattering. Moreover, as a function of increasing temperature the intensity of both dispersionless excitations

decreases strongly as shown in Fig. 3 A–C. This is qualitatively consistent with the thermal population of the first excited crystal-field level and provides further evidence for a magnetic character of these excitations. However, closer inspection reveals that the intensity decreases much faster than would be



**Fig. 3.** Temperature dependence of the CEF and VBS at  $E_{CF} = 4.9$  meV and  $E_{VBS} = 7.9$  meV, respectively. (A) Energy scans at the  $M$  point at (003) for various temperatures. Scans are shifted vertically by 60 counts for clarity. Solid lines represent two independent Gaussians. (B) Integrated intensity of the CEF and vibronic bound state normalized to 3 K. Red dashed lines show the calculated temperature dependence at the  $M$  point for a three- and a four-level system. (C) Selected scans shown in A as fitted with a pure crystal-field model with fixed intensities in a three-level model (dotted lines) and a model based on the BFK model (11) (solid lines). (D) Energy scans through the VBS at the  $\Gamma$  and the  $M$  point. Dark solid lines represent a Gaussian fit to the data. Red shading denotes the background and the pure crystal-field excitation.





level may be expected to decrease. In contrast, the newly created  $|\Gamma_6, 1\rangle$  level increases.

Using similar methods as reported in ref. 14, the coupling constant is roughly determined as  $g_{\text{VBS}} = 0.4 \text{ meV}$  (for details see *SI Appendix*). The reduced intensity of the excitation at  $E_{\text{VBS}} = 7.9 \text{ meV}$  compared with the excitation at  $E_{\text{CF}} = 4.9 \text{ meV}$  implies that the low phonon density of states is just sufficient to reach the threshold for the bound state to become detectable. In fact, it is interesting to speculate whether the weak maximum of the calculated density of states at  $E = 11 \text{ meV}$  is just below such a threshold, characteristic of an incipient VBS.

The ME interactions may also be expected to affect the spectrum of phonon and CEF excitations where they coincide (ref. (60) and *SI Appendix*). Following considerations first reported for  $\text{PrNi}_5$  (39) the Hamiltonian of the ME coupling,  $H_{\text{ME}}^I$ , describes the direct coupling between the deformations of the lattice and the  $4f$  shell. In a group theoretical analysis (64) the energy of the coupled phonon–CEF excitation, which is mediated by quadrupolar interactions, is given by

$$\omega_{q\pm}^2 = \frac{E^2 + \omega_0^2}{2} \pm \sqrt{\left(\frac{E^2 - \omega_0^2}{2}\right)^2 + 16\alpha^2 E \omega_0^2 g_{\text{AC}}}, \quad [1]$$

where  $\omega_{q\pm}$  represents the energies of the two anticrossing excitations;  $\omega_0$  is the phonon energy which depends on  $\mathbf{k}$ ,  $E$  is the nondispersive energy of the CEF level, and  $g_{\text{AC}}$  is an effective coupling constant related to the renormalization of the elastic constant (*SI Appendix*). A fit of our data yields  $g_{\text{AC}} = 12.1(2) \mu\text{eV}$ .

The ME coupling is also reflected in the temperature dependence of the scattering intensity, shown in terms of energy scans at the  $M$  point in Fig. 3A. It is instructive to consider the reduced scattering intensity,  $I/I_0$ , normalized to its value at low temperatures as shown in Fig. 2B for  $E_{\text{CF}} = 4.9 \text{ meV}$  and  $E_{\text{VBS}} = 7.9 \text{ meV}$ . At 200 K we observe a large reduction of the intensity of the crystal-field level at  $E_{\text{CF}}$  by  $\sim 80\%$ , whereas the intensity of the excitation at  $E_{\text{VBS}}$  already vanishes above 100 K. In contrast, a reduction of only 50% would be expected of the intensity at  $E_{\text{CF}}$  for 200 K, when thermally populating the three crystal-field excitations determined in the standard analysis, which ignores the weak mode at  $E_{\text{VBS}}$ . This situation improves slightly with a reduction of 60% at 200 K for four crystal-field levels when additionally taking into account the mode at  $E_{\text{VBS}}$ . However, the agreement is still far from satisfactory.

When additionally considering the coupling to the conduction electrons following the suggestion of ref. 59, a BFK model of crystal-field line broadening (11) provides excellent agreement with our data. The fitting procedure incorporates the code of Keller (66); for technical details see *SI Appendix*. As shown in Fig. 3C the improved account of the peak intensity in the BFK model is also reflected in an improved account of the energy dependence. The associated dimensionless coupling constant  $g_{\text{BFK}} = 0.022(0)$  is proportional to the local exchange constant and density of conduction electron states and remarkably small. While the BFK model already provides a satisfactory

agreement with the broadening, further improvements may be expected when taking into account the interactions with the spectrum of phonons. A full analysis of these contributions is beyond the present capabilities of established computational techniques. As summarized in Table 1, the coupling constants  $g_{\text{VBS}}$  and  $g_{\text{BFK}}$  in  $\text{CeCuAl}_3$  are smaller than in  $\text{CeAl}_2$ . This highlights that the spectrum of low-lying CEF excitations may be modified profoundly, even for systems with rather weak ME coupling.

## Conclusions

In summary, we find two pronounced ME-hybrid excitations in  $\text{CeAuAl}_3$  beyond the Born–Oppenheimer approximation, namely a vibronic bound state and a well-resolved anticrossing. While the former was unexpected in view of previous work which did not detect a VBS in  $\text{CeAuAl}_3$ , the latter represents a property not seen before in any intermetallic compound at zero field. Perhaps most important is the observation that both ME-hybrid excitations are due to acoustic phonons and may be resolved well, even though there is considerable damping of the CEF levels due to particle–hole excitations and the coupling constants are weak. As these observations have been made possible by means of high-resolution single-crystal neutron spectroscopy, which is generally not used in the study of CEF excitations, we conclude that ME-hybrid excitations are much more generic than hitherto assumed and must be abundant in a wide range of materials. The simplicity of our observations provides a tractable point of reference in the development of a predictive understanding of ME instabilities and functionalities in complex materials.

## Materials and Methods

High-quality single-crystal  $\text{CeAuAl}_3$  was grown by optical float zoning under ultrahigh vacuum-compatible conditions (67). High sample purity was confirmed by means of resistivity, magnetization, and specific heat of small pieces cut from the same ingot (52, 68). The correct  $\text{BaNi}_5\text{Sn}_3$ -type structure and high crystalline quality were confirmed by powder and Laue X-ray diffraction as well as neutron diffraction (52). Neutron diffraction established that antisite disorder is negligible in the present samples (52), consistent with a recent NMR study (69).

Inelastic neutron-scattering measurements were carried out on the triple-axis spectrometers PUMA and PANDA at Maier-Leibnitz Zentrum (MLZ), Garching, Germany (70, 71). For the inelastic measurements a single crystal with a mass of 2 g was used. The sample was cooled with a pulse-tube cooler. All data were recorded at a temperature of 5 K unless stated otherwise, i.e., well above  $T_N = 1.3 \text{ K}$ . For details of the experimental setup and the momentum and energy ranges covered in our experiments, refer to *SI Appendix*. The data reported in this paper are available from figshare (72).

Ab initio calculations were carried out using VASP and the frozen-core PAW method (ref. 60 and *SI Appendix*). Taking into account weak interactions of the RE ions with phonons, an expression for the hybridization of quadrupolar interactions and phonons was derived.

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